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Cosmetic composition comprising polymers having original star structure,
for use in preparations for maintaining or fixing hairstyle, or for
treatment of hair -

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Patent Family:

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(54) **Composition cosmétique comprenant des polymères ayant une structure en étoiles et leur utilisation notamment en capillaire**

Kosmetische Zusammensetzungen aus sternförmigen Polymeren und ihre Anwendung insbesondere für Haare

Cosmetic compositions containing star shaped polymers and their use in particular for hair

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5 atomes d'carbon ; un radical aryl ; un radical hétérocycle; étant donné que R²⁰ et R²¹ peuvent être joints de manière à former un cycle, saturé ou insaturé; étant donné que chaque radical peut en outre être substitué avec un radical alkyle ayant 1-6 atomes de carbone, un radical alkoxy ayant 1-6 atomes de carbone ou un radical aryle;

10 (ii) le monoxyde de carbone; les porphyrines et les porphycènes, éventuellement substitués; l'éthylénediamine et le propylénediamine, éventuellement substitués; les multiamines avec amines tertiaires telles que le pentaméthyldiéthylénetriamine; les aminoalcools tels que l'aminoéthanol et l'aminopropanol, éventuellement substitués; les glycols tels que l'éthylèneglycol ou le propylèneglycol, éventuellement substitués; les arènes tels que le benzène, éventuellement substitués; le cyclopentadiène, éventuellement substitué; les pyridines et bipyridines, éventuellement substituées; l'acetonitrile; la 1,10-phénanthroline; les cryptands et les éthers-couronnes; la spartéine.

15 6. Composition selon l'une des revendications précédentes, dans laquelle l'agent propulseur est choisi parmi, seul ou en mélange, les hydrocarbures volatils tels que le n-butane, le propane, l'isobutane, le pentane, un hydrocarbure chloré et/ou fluoré; le gaz carbonique, le protoxyde d'azote, le diméthyléther (DME), l'azote, l'air comprimé.

20 7. Composition selon l'une des revendications précédentes, dans laquelle l'agent auxiliaire de filmification est choisi parmi, seul ou en mélange :

- les glycols et leurs dérivés tels que le diéthylène glycol éthyléther, le diéthylène glycol méthyléther, le diéthylène glycol butyléther, le diéthylène glycol hexyléther, l'éthylène glycol éthyléther, l'éthylène glycol butyléther, l'éthylène glycol hexyléther;
- les esters de glycérol, tels que le diacétate de glycérol et le triacétate de glycérol;
- les dérivés de propylène glycol et en particulier le propylène glycol phényléther, le propylène glycol diacétate, le propylène glycol méthyléther, le propylène glycol éthyléther, le propylène glycol butyléther, le dipropylène glycol méthyléther, le dipropylène glycol butyléther, le di-propylène glycol éthyléther, le tripropylène glycol butyléther, le tripropylène glycol méthyléther;
- des esters d'acids notamment carboxyliques, tels qu' des citrates, des phtalates, des adipates, des carbonates, des tartrates, des phosphates, des sébaçates,

25 - des dérivés oxyéthylénés tels que les huiles oxyéthylénées, notamment les huiles végétales telles que l'huile de ricin; les huiles de silicium oxyéthylénées.

30 8. Composition selon l'une des revendications précédentes, dans laquelle le polymère de structure 'en étoiles' est présent en une quantité comprise entre 1-95% en poids de matière sèche, par rapport au poids total de la composition, de préférence entre 1-50% en poids et préférentiellement entre 1-20% en poids.

35 9. Composition selon l'une des revendications précédentes, dans laquelle le polymère de structure 'en étoiles' est présent dans le milieu sous forme dissoute ou en dispersion, dans une phase aqueuse, organique ou hydroorganique notamment alcoolique ou hydroalcoolique.

40 10. Composition selon l'une des revendications précédentes, se présentant sous la forme d'un spray, d'une laque, d'une mousse, de crème, de gel, d'émulsion, de lotion ou de cire.

45 11. Procédé de maintien ou de mise en forme des cheveux, **caractérisé par le fait qu'il** consiste à appliquer sur ceux-ci une composition cosmétique selon l'une des revendications précédentes.

50 12. Utilisation d'une composition cosmétique selon l'une des revendications 1 à 10, pour la fabrication d'un produit cosmétique capillaire destiné à maintenir et/ou fixer et/ou traiter la coiffure et/ou les cheveux.

55 13. Utilisation selon la revendication 12, pour la fabrication d'un produit de coiffage tel qu'une laque, un spray ou une mousse, en vue d'obtenir le maintien ou la mise en forme de la coiffure.

45 **Claims**

1. Hair cosmetic composition, in particular for the treatment and/or the fixing of the hair, comprising, in a cosmetically acceptable medium comprising at least one constituent chosen from water; one or more cosmetically acceptable solvents, such as alcohols comprising 1 to 4 carbon atoms, ethers, ketones or C₁-C₃ lower carboxylic acid esters; cosmetic active principles; softeners; antioxidants; opacifiers; antifoaming agents; preservatives; sequestering agents; UV screening agents; ceramides; antidandruff agents; complexing agents; agents for dramatic hair loss; antifungal or antisep-

tic agents; thickeners; fixing or nonfixing polymers; conditioners; propellants; basifying or acidifying agents; hydrophilic polymers; film-forming polymers, in particular in aqueous dispersion; surfactants, in particular anionic or nonionic surfactants, optionally comprising silicone groups; or an additional agent which is able to form a film, such as a plasticizing agent and/or a coalescence agent; at least one polymer with a "star" structure capable of being obtained by atom transfer radical polymerization.

- of one or more radically polymerizable monomers, chosen from:

(i) acrylic or methacrylic esters obtained from linear, branched or cyclic aliphatic alcohols and/or from aromatic alcohols comprising 1 to 20 carbon atoms, such as methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, isobutyl (meth)acrylate or tert-butyl (meth)acrylate;
 (ii) C₁-C₄ hydroxyalkyl (meth)acrylates, such as 2-hydroxyethyl (meth)acrylate, or 2-hydroxypropyl (meth)acrylate;
 (iii) ethylene glycol, diethylene glycol or polyethylene glycol (meth)acrylates with a hydroxyl or ether end;
 (iv) vinyl, allyl or methallyl esters obtained from linear or branched C₁-C₁₀ or cyclic C₁-C₆ aliphatic alcohols and/or from C₁-C₆ aromatic alcohols, such as vinyl acetate, vinyl propionate, vinyl benzoate or vinyl tert-butylbenzoate;
 (v) N-vinylpyrrolidone; vinylcaprolactam; vinyl-N-alkylpyrroles having 1 to 6 carbon atoms; vinyloxazoles; vinylthiazoles; vinylpyrimidines; vinylimidazoles; or vinyl ketones;
 (vi) (meth)acrylamides obtained from linear, branched or cyclic aliphatic amines and/or from aromatic amines comprising 1 to 20 carbon atoms, such as tert-butylacrylamide; or (meth)acrylamides, such as acrylamide, methacrylamide or di(C₁-C₄)alkyl (meth)acrylamides;
 (vii) olefins, such as ethylene, propylene, styrene or substituted styrene;
 (viii) fluorinated or perfluorinated acrylic or vinyl monomers, in particular (meth)acrylic esters with perfluoroalkyl units;
 (ix) monomers comprising an amine functional group in the free or else partially or completely neutralized or else partially or completely quaternized form, such as dimethylaminoethyl (meth)acrylate, dimethylaminoethylmethacrylamide, vinyl

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amine, vinylpyridine or diallyldimethylammonium chloride;

(x) carboxybetaines or sulphobetaines obtained by partial or complete quaternization of monomers comprising thienic unsaturation comprising an amine functional group by sodium salts of carboxylic acids comprising a mobile halide (sodium chloroacetate, for example) or by cyclic sulphones (propane sulphone);
 (xi) silicone-comprising (meth)acrylates or (meth)acrylamides, in particular (meth)acrylic esters comprising siloxane units;
 (xii) their mixtures;

in the presence

- of an initiator having at least two atoms and/or groups radically transferable by polymerization;
- of a compound comprising a transition metal, capable of participating in a reduction stage with the initiator and a "dormant" polymer chain, chosen from those of formula Mⁿ⁺X'_n, in which:

- M is chosen from Cu, Au, Ag, Hg, Ni, Pd, Pt, Rh, Co, Ir, Fe, Ru, Os, Re, Mn, Cr, Mo, W, V, Nb, Ta and Zn, and
- X' represents a halogen (in particular bromine or chlorine), OH, (O)_{1/2}, an alkoxy radical having 1-6 carbon atoms, (SO₄)_{1/2}, (PO₄)_{1/3}, (HPO₄)_{1/2}, (H₂PO₄) and a triflate, hexafluorophosphate, methanesulphonate, arylsulphonate, SeR, CN, NC, SCN, CNS, OCN, CNO, N₃ and R'CO₂, in which R represents an aryl or linear or branched alkyl radical having 1-20, preferably 1-10, carbon atoms and R' represents H or a linear or branched alkyl radical having 1-6 carbon atoms or an aryl radical which is optionally substituted by one or more halogen atoms, in particular fluorine and/or chlorine atoms;

- n is the charge on the metal;

and

- of a ligand chosen from:

- (i) compounds comprising at least one nitrogen (N), oxygen (O) phosphorus (P) and/or sulphur (S) atom which are capable of coordinating via a σ bond to the said compound comprising a transition metal;
- (ii) compounds comprising at least two carbon atoms capable of coordinating via a π

bond to the said compound comprising a transition metal;

(iii) compounds comprising at least one carbon atom capable of coordinating via a σ bond to the said compound comprising a transition metal but which do not form a carbon-carbon bond with the monomer during the polymerization;

(iv) compounds capable of coordinating via a μ or η bond to the said compound comprising a transition metal;

the said polymer comprising one or more monomers M_i , the corresponding homopolymer of which exhibits a T_g of greater than or equal to 10°C , preferably greater than or equal to 15°C and even better still of greater than or equal to 20°C ; this or these monomers M_i being present, in the final polymer, in an amount of between 55 and 95% by weight, preferably in an amount of 60 to 93% by weight and even better still in an amount of 65 to 90% by weight, with respect to the total weight of monomers; and the said polymer furthermore comprising one or more monomers M_j , the corresponding homopolymer of which exhibits a T_g of less than or equal to 10°C , preferably of less than or equal to 5°C and even better still of less than or equal to 0°C ; this or these monomers M_j being present, in the final polymer, in an amount of between 5 and 45% by weight, preferably in an amount of 7 to 40% by weight and even better still in an amount of 10-35% by weight, with respect to the total weight of monomers.

2. Composition according to the preceding claim, in which the monomers are chosen from:

- (meth)acrylic esters obtained from linear or branched aliphatic alcohols, preferably C_1 - C_{20} alcohols;
- C_1 - C_{20} (meth)acrylic esters comprising perfluoroalkyl units;
- C_1 - C_{20} (meth)acrylic esters comprising siloxane units;
- (meth)acrylamides obtained from linear, branched or cyclic aliphatic amines and/or from aromatic amines preferably comprising 1 to 20 carbon atoms, such as tert-butylacrylamide; or (meth)acrylamides, such as acrylamide, methacrylamide or di(C_1 - C_4)alkyl(meth)acrylamides;
- vinyl, allyl or methallyl esters obtained from linear or branched C_1 - C_{10} or cyclic C_1 - C_6 aliphatic alcohols;
- vinylcaprolactam;
- optionally substituted styrene;
- their mixtures.

3. Composition according to one of the preceding claims, in which the initiator is chosen from the compounds of formula:

- 5 - $R^{11}_x R^{12}_y R^{13}_z C-(RX)_t$, in which x, y and z represent an integer ranging from 0 to 4, t an integer ranging from 1 to 4, and $x+y+z = 4-t$;
- $R^{13}_x C_6-(RX)_y$ (saturated ring with 6 carbons), in which x represents an integer ranging from 7 to 11, y represents an integer ranging from 1 to 5, and $x+y = 12$;
- $R^{13}_x C_6-(RX)_y$ (unsaturated ring with 6 carbons), in which x represents an integer ranging from 0 to 5, y represents an integer ranging from 1 to 6, and $x+y = 6$;
- $[-(R^{11})(R^{12})(R^{13})C-(RX)]_n$, in which n is greater than or equal to 1; cyclic or linear;
- $[-(R^{12})_x C_6(RX)_y R^{11}]_n$, in which x represents an integer ranging from 0 to 6, y represents an integer ranging from 1 to 6 and n is greater than or equal to 1, with $x+y = 4$ or 6; cyclic or linear;
- $[-(R^{12})_x C_6(RX)_y R^{11}]_n$, in which x represents an integer ranging from 0 to 12, y represents an integer ranging from 1 to 12 and n is greater than or equal to 1, with $x+y = 10$ or 12; cyclic or linear;
- $[-OSi(R^{11})_x(RX)_y]_n$, cyclic or linear, in which x and y represent an integer ranging from 0 to 2 and n is greater than or equal to 1, with $x+y = 2$;
- $R^{11}N-X_2$
- $(R^{11})_x P(O)_y-X_{3-x}$, in which x and y represent integers ranging from 0 to 2 and $x+y = 5$;
- $(R^{11}O)_x P(O)_y-X_{3-x}$, in which x and y represent integers ranging from 0 to 2 and $x+y = 5$;
- $[-(R^{11})_t N_z P(O)_x(O-RX)_y]_n$, cyclic or linear, in which x represents an integer ranging from 0 to 4, y represents an integer ranging from 1 to 5, z represents an integer ranging from 0 to 2, t represents an integer ranging from 0 to 3 and n is greater than or equal to 1;

in which:

- R, R^{11} , R^{12} and R^{13} represent, independently of one another, a hydrogen or halogen atom; a linear or branched alkyl radical having 1-20, preferably 1-10 and more preferably 1-6 carbon atoms; a cycloalkyl radical having 3-8 carbon atoms; a $-C(=Y)R^5$, $-C(=Y)NR^6R^7$ or $-R^8_3Si$ radical; $-COCl$; $-OH$; $-CN$; an alkenyl or alkynyl radical having 2-20, preferably 2-6, carbon atoms; an oxiranyl or glycidyl radical or an alkylene or alkenylene radical substituted with an oxiranyl or a glycidyl; an aryl, heterocycl, aralkyl or aralkenyl radical; or an alkyl radical having 1-6 carbon atoms in which all or part of the hydrogen atoms are substituted either by halogen atoms, such as fluorine, chlorine or

bromine, or by an alkoxy group having 1-4 carbon atoms or by an aryl, heterocycl, $-C(=Y)R^5$, $-C(=Y)NR^6R^7$, oxiranyl or glycidyl radical; X represents a halogen atom, such as Cl, Br or I, or an $-OR$, $-SR$, $-SeR$, $-OC(=O)R'$, $-OP(=O)R'$, $-OP(=O)(OR')_2$, $-OP(=O)OR'$, $-O-NR'_2$, $-S-C(=S)NR'_2$, $-CN$, $-NC$, $-SCN$, $-CNS$, $-OCN$, $-CNO$ or $-N_3$ radical, in which R' represents an alkyl radical having 1-20 carbon atoms which is optionally substituted by one or more halogen atoms, in particular fluorine and/or chlorine atoms, and R represents a linear or branched alkyl or aryl radical having 1-20, preferably 1-10, carbon atoms, it additionally being possible for the $-NR'_2$ group to represent a cyclic group, the two R' groups being joined so as to form a 5-, 6- or 7-membered heterocycle; Y represents O, S or NR^8 (preferably O); R^5 represents a linear or branched alkyl, alkylthio or alkoxy radical having 1-20 carbon atoms; an OH radical; an OM' radical with M' = alkali metal; an aryloxy radical or a heterocyclyoxy radical; R^6 and R^7 represent, independently of one another, H or a linear or branched alkyl radical having 1-20 carbon atoms; it being given that R^6 and R^7 can be joined to form an alkylene group having 2-7, preferably 2-5, carbon atoms; R^8 represents H; a linear or branched alkyl radical having 1-20 carbon atoms or an aryl radical.

4. Composition according to one of the preceding claims, in which the initiator is chosen from:

- octa(2-isobutyrylbromide)-octa(tert-butyl)calix(8)arene,
- octa(2-propionylbromide)-octa(tert-butyl)calix(8)arene, and
- hexakis(α -bromomethyl)benzene.

5. Composition according to one of the preceding claims, in which the ligand is chosen from:

(i) the compounds of formula: $R^9-Z-(R^{14}-Z)_m-R^{10}$ or $R^{20}R^{21}C[C(=Y)R^5]$ in which:

- R^9 and R^{10} are, independently of one another, a hydrogen atom; a linear or branched alkyl radical having 1-20, preferably 1-10, carbon atoms; an aryl radical; a heterocycl radical; or an alkyl radical having 1-6 carbon atoms which is substituted with an alkoxy radical having 1-6 carbon atoms or a dialkylamino radical having 1-4 carbon atoms or a $-C(=Y)R^5$ or $-C(=Y)NR^6R^7$ and/or $YC(=Y)R^8$ radical, R^5 to R^8 and Y having the definitions given in Claim 3; it being given that R^9 and R^{10} can be joined so as to form a saturated or unsaturated ring;
- R^{14} represents, independently of one another, a divalent group chosen from alkanediyls having 2-4 carbon atoms; alkenediyls having 2-4 carbon atoms; cycloalkanediyls having 3-8 carbon atoms; cycloalkenediyls having 3-8 carbon atoms; arenediyls and heterocyclyenes;
- Z represents O, S, NR^{15} or PR^{15} , with R^{15} representing H; a linear or branched alkyl radical having 1-20 carbon atoms; an aryl radical; a heterocycl radical; or an alkyl radical having 1-6 carbon atoms which is substituted with an alkoxy radical having 1-6 carbon atoms or a dialkylamino radical having 1-4 carbon atoms or a $-C(=Y)R^5$ or $-C(=Y)NR^6R^7$ and/or $YC(=Y)R^8$ radical (R^5 to R^8 and Y having the definitions given in Claim 3);
- m is between 0 and 6;
- R^{20} and R^{21} are, independently of one another, a hydrogen atom; a halogen atom; a linear or branched alkyl radical having 1-20, preferably 1-10, carbon atoms; an aryl radical; or a heterocycl radical; it being given that R^{20} and R^{21} can be joined so as to form a saturated or unsaturated ring; it being given that, in addition, each radical can be substituted with an alkyl radical having 1-6 carbon atoms, an alkoxy radical having 1-6 carbon atoms or an aryl radical;
- (ii) carbon monoxide; optionally substituted porphyrins and porphycenes; optionally substituted ethylenediamine and propylenediamine; polyamines with tertiary amines, such as pentamethyldiethylenetriamine; aminoalcohols, such as aminoethanol and aminopropanol, which are optionally substituted; glycols, such as ethylene glycol or propylene glycol, which are optionally substituted; arenes, such as benzene, which are optionally substituted; optionally substituted cyclopentadiene; optionally substituted pyridines and bipyridines; acetonitrile; 1,10-phenanthroline; cryptands and crown ethers; or sparteine.

6. Composition according to one of the preceding claims, in which the propellant is chosen from, alone or as a mixture, volatile hydrocarbons, such as n-butane, propane, isobutane, pentane or a chlorinated and/or fluorinated hydrocarbon; carbon dioxide gas, nitrous oxide, dimethyl ether (DME), nitrogen or compressed air.

7. Composition according to one of the preceding claims, in which the additional agent which is able to form a film is chosen from, alone or as a mixture:

- glycols and their derivatives, such as diethylene glycol ethyl ether, diethylene glycol methyl ether, diethylene glycol butyl ether, diethylene glycol hexyl ether, ethylene glycol ethyl ether, ethylene glycol butyl ether or ethylene glycol hexyl ether;
- glycerol esters, such as glyceryl diacetate and glyceryl triacetate;
- propylene glycol derivatives and in particular propylene glycol phenyl ether, propylene glycol diacetate, propylene glycol methyl ether, propylene glycol ethyl ether, propylene glycol butyl ether, dipropylene glycol methyl ether, dipropylene glycol butyl ether, dipropylene glycol ethyl ether, tripropylene glycol butyl ether or tripropylene glycol methyl ether;
- acid esters, in particular carboxylic acid esters, such as citrates, phthalates, adipates, carbonates, tartrates, phosphates or sebacates,
- oxyethylenated derivatives, such as oxyethylenated oils, in particular vegetable oils, such as castor oil; or oxyethylenated silicone oils.

8. Composition according to one of the preceding claims, in which the polymer with the "star" structure is present in an amount of between 1-95% by weight on a dry basis, with respect to the total weight of the composition, preferably between 1-50% by weight and preferentially between 1-20% by weight.

9. Composition according to one of the preceding claims, in which the polymer with the "star" structure is present in the medium in the form dissolved or in dispersion in an aqueous, organic or aqueous/organic phase, in particular an alcoholic or aqueous/alcoholic phase.

10. Composition according to one of the preceding claims, which is provided in the form of a spray, lacquer, foam, cream, gel, emulsion, lotion or wax.

11. Process for the form retention or shaping of the hair, characterized in that it consists in applying, to the latter, a cosmetic composition according to one of the preceding claims.

12. Use of a cosmetic composition according to one of Claims 1 to 10 in the manufacture of a hair cosmetic product intended to retain the form of and/or fix and/or treat the hairstyle and/or the hair.

13. Use according to Claim 12 in the manufacture of a styling product, such as a lacquer, a spray or a foam, for the purpose of obtaining form retention or

shaping of the hairstyle.

Patentansprüche

5 1. Kosmetische Zusammensetzung für das Haar, insbesondere zur Behandlung und/oder Fixierung der Haare, die in einem kosmetisch akzeptablen Medium mindestens einen Bestandteil, der unter den folgenden Verbindungen ausgewählt ist: Wasser; einem oder mehreren kosmetisch akzeptablen Lösungsmitteln, wie C₁₋₄-Alkoholen, Ethern, Ketonen, Estern von niederen Carbonsäuren mit 1 bis 3 Kohlenstoffatomen; kosmetischen Wirkstoffen; reizlindernden Wirkstoffen, Antioxidantien, Trübungsmittern, Schaumverhüttungsmitteln, Konservierungsmitteln, Maskierungsmitteln, UV-Filtern, Ceramiden; Antischuppenmitteln; Komplexbildnern; Wirkstoffen gegen Haarausfall; antimykotischen oder antiseptischen Wirkstoffen; Verdickungsmitteln, fixierenden oder nichtfixierenden Polymeren oder Konditioniermitteln; Treibmitteln, Alkalisierungsmitteln oder Ansäuерungsmitteln; hydrophilen Polymeren; filmbildenden Polymeren, insbesondere in wässriger Dispersion; grenzflächenaktiven Stoffen und insbesondere anionischen oder nichtionischen grenzflächenaktiven Stoffen, die ggf. siliconhaltig sind; Hilfsmitteln zur Filmbildung wie Weichmacher und/oder Koaleszenzmitteln; und mindestens ein Polymer mit "sternförmiger" Struktur enthält, das erhältlich ist durch radikalische Atomtransferpolymerisation:

10 - eines oder mehrerer radikalisch polymerisierbarer Monomere, die ausgewählt sind unter:

15 (i) den Acrylestern oder Methacrylestern, die ausgehend von aliphatischen, geradkettigen, verzweigten, cyclischen und/oder aromatischen Alkoholen vorzugsweise mit 1 bis 20 Kohlenstoffatomen hergestellt werden, wie beispielsweise Methyl(meth)acrylat, Ethyl(meth)-acrylat, Propyl(meth)acrylat, Butyl(meth)acrylat, Isobutyl(meth)acrylat und t-Butyl(meth)acrylat;

20 (ii) C₁₋₄-Hydroxyalkyl(meth)acrylaten, wie 2-Hydroxyethyl(meth)acrylat oder 2-Hydroxypropyl(meth)acrylat;

25 (iii) Ethylenglykol(meth)acrylaten, Diethylenglykol(meth)acrylaten und Polyethylenglykol(meth)-acrylaten mit endständigen Hydroxy- oder Ethergruppen;

30 (iv) Vinyl estern, Allylestern oder Methallylestern, die ausgehend von aliphatischen, geradkettigen oder verzweigten C₁₋₁₀-Al-

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